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Study of hydrogen diffusion in superprotonic ionic conductors, $MHXO_4$, by μ^+ SR and QENS

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ABSTRACT

In order to clarify the mechanism of high proton conductivity (σ_{H^+}) for superprotonic ionic conductors, $MHXO_4$, where $M=Cs$ and Rb , $X=S$ and Se , muon-spin rotation and relaxation (μ^+ SR) and quasi-elastic neutron scattering (QENS) measurements have been performed at temperatures mainly in the vicinity of T_c , at which $MHXO_4$ undergoes a structural phase transition from a low- T orthorhombic phase (Phase II) to a high- T tetragonal phase (Phase I). The μ^+ SR experiment shows the presence of muonium (Mu) state even in Phase I only for $CsHSO_4$ (CHS), while no Mu state was found in Phase I of $CsHSeO_4$ (CHSe). Considering the fact that the σ_{H^+} in Phase I of CHS is more than 10 times larger than that of CHSe, this implies a relationship between the presence of the atomic hydrogen (Mu) state and high σ_{H^+} in Phase I of CHS. According to the QENS measurements using a single crystal of CHSe, line shapes of the energy spectra along three crystallographic directions are found to be slightly anisotropic in Phase I, in contrast to the isotropic conductivity reported by AC conductivity measurements.

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1. Introduction

Cesium hydrogen sulfate, $CsHSO_4$ (CHS), and related materials, $MHXO_4$, where $M=Rb$, K and $X=S$, Se , are considered to be promising candidates for the solid electrolyte of fuel cells operated in intermediate region of temperature from 300 to 600 K [1]. This is because $MHXO_4$ exhibits extraordinarily high proton conductivity (σ_{H^+}) at temperatures above its first order structural phase transition from a low- T monoclinic phase (Phase II) to a high- T tetragonal phase (Phase I) ($T_c=414$ K for CHS). It is known that σ_{H^+} leaps by four orders of magnitude at T_c with increasing T [2]. Phase I is therefore called the “superprotonic” conducting (SPC) phase.

Several experiments, such as 1H -NMR measurement [3], powder neutron diffraction for $CsDSO_4$ [4] and quasi-elastic neutron scattering (QENS) for CHS using powder samples [5] have been carried out, and also computations of proton diffusion (PD) processes using density functional theory [6] were made in order to investigate the mechanism of the high σ_{H^+} in Phase I

of CHS. It has been reported that there are two PD paths in CHS; one is the PD via hydrogen bond between the first nearest neighbor (FNN) sulfate tetrahedra, SO_4^{2-} , and the other is a direct diffusion between the second nearest neighbor (SNN) SO_4^{2-} [5,6]. In order to realize the practical use of CHS as the electrolyte for the fuel cell, it is essential to improve performance of CHS as a solid electrolyte. In particular, it is necessary to increase σ_{H^+} and to decrease T_c . For this purpose we need detailed information on the PD in CHS, such as which path is the dominant process for the proton motion, and what is the key process for σ_{H^+} in Phase I of CHS.

In order to clarify the detailed mechanism responsible for the high σ_{H^+} of $MHXO_4$, positive muon-spin rotation and relaxation (μ^+ SR) and QENS experiments have been performed at temperatures mainly in the vicinity of T_c . Both techniques provide us complementary information on proton diffusive properties, because their time scales for detectable diffusive motion are 10^{-5} to 10^{-9} s for μ^+ SR and 10^{-9} to 10^{-13} s for QENS, respectively. Particularly, in order to elucidate the existence/absence of anisotropic σ_{H^+} , we have prepared single crystal samples of $MHXO_4$. In this paper, we focus on the results of μ^+ SR measurements for CHS and $CsHSeO_4$ (CHSe), and QENS experiments on CHSe.

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2. Experimental

Single crystal samples of MHXO_4 were grown by a slow evaporation method at ambient T from an aqueous solution [7]. The μ^+ SR experiments were performed on the πA spectrometer at KEK and on EMU at the ISIS Pulsed Muon Facility at the Rutherford Appleton Laboratory using pulsed surface muon beam. Experimental setup and techniques were described elsewhere [8]. The QENS experiment on single crystal CHSe was carried out using the Disk Chopper time-of-flight Spectrometer (DCS) at the NIST Center for Neutron Research (NCNR) [9] with a wavelength of 9 Å and energy resolution of ~ 10 μeV half width at half maximum (HWHM). The single crystal sample of CHSe was wrapped in aluminum foil, and then inserted into a Pb-sealed aluminum-cell under ambient He gas environment. The sample was measured in the temperature range between 410 K and 470 K. To detect anisotropic PD, time-of-flight spectra along [100], [001], and [110] directions were measured. The measured data were converted to energy spectra as a function of Q using the DAVE software of NCNR [10].

3. Results and discussion

Zero-field (ZF) and longitudinal-field (LF) μ^+ SR measurements for CHS were performed as a function of temperature in the temperature range from 250 to 450 K to explore the dynamics of muons in CHS as a radioactive tracer of H^+ . ZF time spectra exhibit slow Gaussian type relaxation. The relaxation behavior is almost decoupled by applying LF less than 10^{-2} T. This indicates that the muons feel nuclear dipole field caused by randomly distributed Cs and H^+ . Both ZF and LF μ^+ SR spectra were well fitted by a dynamic Kubo–Toyabe (KT) function using common parameters, the muon hopping rate (ν_μ) and field distribution width (Δ_{KT}) at each T [8]. Fig. 1 shows the dependences of KT parameters, ν_μ and Δ_{KT} on inverse T . The T dependence of ν_μ is found to be two orders of magnitude larger than that of Δ_{KT} in the whole T range measured. As T increases from ambient T , the $\nu_\mu(T)$ curve exhibits an abrupt increase at T_c , corresponding to the T dependence of σ_{H^+} . Assuming the Arrhenius relation, the activation energies of ν_μ in Phase I, $E_{a,I}$ and Phase II, $E_{a,II}$, are estimated as $E_{a,I}=0.01$ eV and $E_{a,II}=0.1$ eV, respectively. This is

qualitatively in good agreement with values from the calculation and σ_{H^+} measurements, although these values are rather small for those evaluated from conductivity measurements of H^+ . The difference could be explained by the mass effect between the H^+ and the μ^+ .

Fig. 2 shows normalized initial asymmetries (A_{TF}) of the weak transverse-field (wTF) μ^+ SR spectra for CHS and CHSe as a function of T . For both samples, as T increases from ambient T , the A_{TF} gradually increases up to T_c , and then A_{TF} exhibits a sudden increase at T_c , and finally levels off to a constant value with further increasing T . It should be noted that the A_{TF} of CHS does not reach its full value ($=1$) even in Phase I, while A_{TF} for CHSe is 1.0 above T_c . In most cases for non-magnetic insulators, the missing fraction of A_{TF} means that some of the embedded μ^+ couple with electrons, forming muonium (Mu) [8]. The $A_{\text{TF}}(T)$ behavior therefore shows that Mu fraction in Phase I is found only in CHS, while Mu is not formed in Phase I of CHSe. In addition, high LF measurements up to 0.45 T for CHS show a clear decoupling curve due to the presence of the triplet Mu state and a fast relaxation remains even in 0.45 T. This means that Mu is found to be diffusing very rapidly and also that Mu is thought to be converted to μ^+ quickly [11]. Considering these results, this implies that Mu's, i.e., atomic hydrogens, are likely to exist even in the SPC phase of CHS. One would deduce a relationship between the presence of atomic hydrogen state and high σ_{H^+} of CHS.

By QENS measurements for CHSe, it is found that each spectrum consists of two Lorentzian components, one “narrow” and the other one “wide”. The HWHM of the narrow component is of the order of μeV and that of the wide component is ~ 100 μeV . A typical reduced energy spectrum for CHSe at 425 K, and the two Lorentzian components, are shown in Fig. 3. The spectrum was well fitted using a combination of the two Lorentzian function convoluted with the instrument resolution function. The Q dependences of the HWHMs of both components at 410 K are shown in Fig. 4. The HWHM curves for both components show clear anisotropic behavior in the three directions, [110], [100], and [001]. The HWHMs of the narrow components for the all directions exhibit monotonic increases with increasing Q up to 0.7 \AA^{-1} . The slope of the HWHM along the [110] direction seems to be larger than those along the other two directions, indicating anisotropic PD in Phase I of CHSe. Since, in the small Q region, the slope of HWHM as a function of Q^2 in a given directions is directly proportional to the diffusion constant along that direction [12],

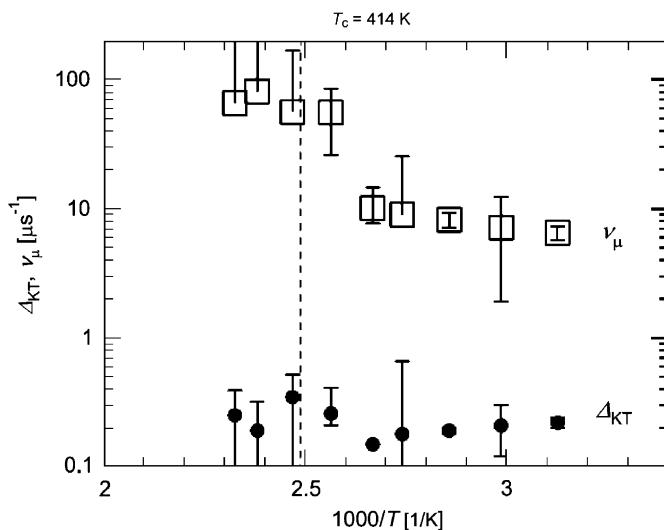


Fig. 1. The fitting results of ZF and LF μ^+ SR spectra for CHS using dynamic KT function. In this and subsequent figures, error bars represent \pm one standard deviation.

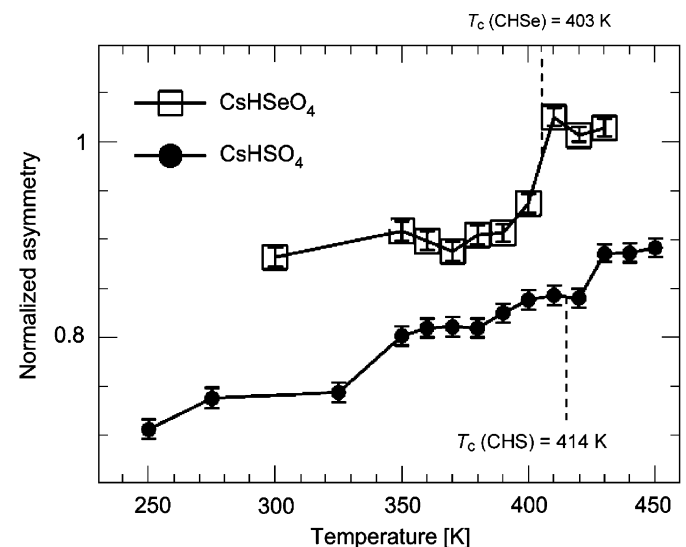


Fig. 2. Temperature dependence of normalized asymmetry of wTF μ^+ SR spectra for CHS and CHSe.

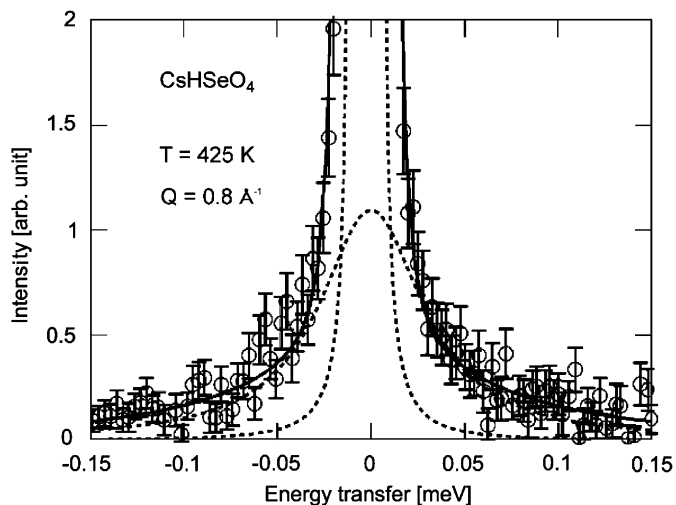


Fig. 3. A typical QENS spectrum for CHSe at 425 K. Dotted lines show the fitting results of the two Lorentzian components.

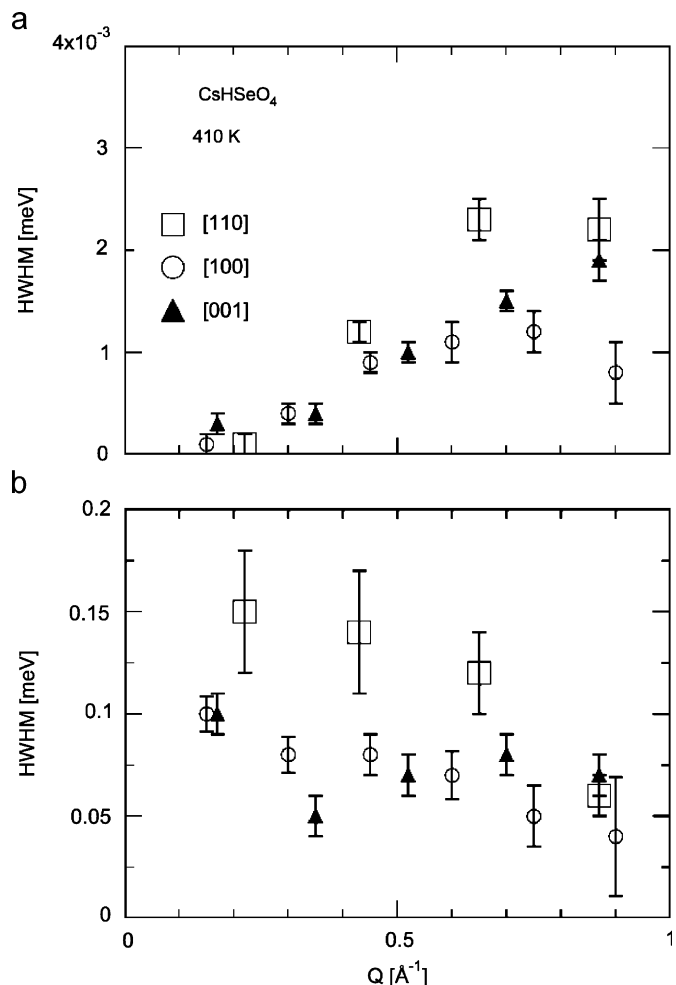


Fig. 4. Q dependences of HWHM of the two Lorentzian components of the QENS spectra in three crystallographic directions of CHSe. (a) Narrow component and (b) wide component.

the diffusion constant along the [110] direction appears to be larger than the diffusion constant for the other two directions. Unfortunately, the energy resolution of the instrument of the

present study would not be enough to quantitatively discuss the HWHM of the narrow component. We need to perform additional QENS experiments for CHS using higher energy resolution instrument, such as back-scattering spectrometer.

Finally, we should mention the relationship between μ^+ SR and QENS results. The HWHMs, which are obtained from QENS measurements, should correspond to the jump rates of the proton hopping, of the order of 100 MHz for the narrow component and 10 GHz for the wide component, respectively. Since the muon hopping rate observed in Phase I of CHS is ~ 100 MHz, the muon hopping would be assigned to the proton hopping represented by the narrow component in the QENS spectrum. But the fast proton motion observed by QENS measurement is too fast to detect by μ^+ SR. Although the narrow component of the QENS spectra was assigned to the hopping between SNN sulfate by the powder QENS measurements [4], our preliminary calculations for the QENS spectrum of single crystal CHSe sample using extended Chudley–Elliott model [12] suggest that the narrow component represents the hopping between FNN sulfate [11]. However, in order to discuss the detailed proton motion, we need to calculate using a refined model of the proton motion. The Mu site and its dynamics, and the relationship to QENS results are also issues that remain to be solved by further study of Phase I of CHS.

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